The solubility of quartz in the aqueous sodium chloride solution at high temperatures and high pressures

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THE SOLUBILITY OF QUARTZ IN THE AQUEOUS SODIUM CHLORIDE SOLUTION AT HIGH TEMPERATURES AND HIGH PRESSURES

BY SHIGETO KITAHARA

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The solubility of quartz in the aqueous solutions of 1, 3 and 7% sodium chloride concentration was measured at the temperatures up to 500°C and at the packing ratios from 1/3 to 1/1.6 ml/ml by observing the loss in the weight of quartz blocks in contact with the solution. The solubility of quartz in sodium chloride solution was larger than in water at temperatures above 280°C, and rose more rapidly with temperature than in water. Reproducible values were not always obtained at temperatures above 340°C to the critical temperature in the same conditions, and the solubility values were roughly classified into three groups, higher, lower and intermediate. The results under supercritical conditions being considered as the effect of sodium chloride on the solubility of quartz in steam, it is shown that the smaller the density of steam is, the larger the effect of sodium chloride, and the effect can not be found when the density is sufficiently large. As the results the author gave some consideration on the effect of sodium chloride on the equilibrium in the quartz-water system.

Introduction

The solubility of quartz in aqueous solution of sodium chloride at high temperatures and pressures is more important than that in water from the geochemical standpoint, because the so-called "Hydrothermal solution" in geology is not pure water but a dilute solution. The solubility values of quartz in aqueous sodium chloride solution have not been systematically reported. It has been reported that the solubility in sodium chloride solution was not larger than that in water at the conditions that temperature was 500°C, and pressure 500 bars by J. Wyart *et al.*[1] and temperatures, 350, 400°C, pressure 3000 kg/cm² by N. I. Khitarov[2]. In the present investigation the solubility values in sodium chloride solution were observed in the three-phase field, quartz-gas-liquid, and under supercritical conditions. The results of the measurements were obviously greater than those in water.

Experimentals

The samples, the apparatus and the procedures were the same as in the investigation of

1) J. Wyart and G. Sabatier, *Compt. rend.*, **240**, 2157 (1955)
2) N. I. Khitarov, *Geokhimiya*, **1**, 62 (1956)

the solubility of quartz in water at high temperatures and pressures[3]. The aqueous solution of sodium chloride in the present investigation was prepared by solving the special high-grade commercial sodium chloride in distilled water. Concentrations of sodium chloride solution were 1, 3 and 7%.

Time of reaction for equilibrium was the same as in the investigation of the solubility of quartz in water. It was confirmed that the time was sufficient for equilibrium to be established.

Temperature and packing ratio in the three-phase field The range of experimental temperature was from 140°C to those as close as possible to the critical temperature for each concentration of sodium chloride solution. The critical temperatures were obtained from the data reported by A. Olander *et al.*[4] They are shown in Table 1. The packing ratio was

Table 1 Critical temperature of aqueous NaCl solutions

Concentration, %	0	1	3	7
Temperature, °C	374	388.5	408.5	437.5
Pressure, kg/cm²	224	259	309	397

taken such that the liquid and gas phases might coexist in equilibrium state and the sodium chloride concentration of the liquid phase might be as same as possible with the initial one; the values which are reasonable for these conditions are given by the P–V–T relations of water[5] below 370°C, and above 370°C by the phase diagram of NaCl–H_2O system reported by A. Olander *et al.*[4] and the pressure-density relations of NaCl–H_2O system by C. S. Copeland *et al.*[6] They are shown in Table 2.

Table 2 Packing ratio of aqueous NaCl solutions

Temp., °C \ Conc., %		1	3	7
below	350	0.50	0.50	0.50
	360	0.40	0.40	0.40
	370	0.30	—	—
	380	0.32	0.41	0.50
	400		0.41	0.50
	420			0.50

Temperature and packing ratio under the supercritical conditions Experimental temperature was above the critical one to 500°C. Packing ratio was 1/3～1/1.6 ml/ml.

In such conditions the sodium chloride solutions of each concentration consist of only the gas phase according to the phase diagram of NaCl–H_2O system by A. Olander *et al.*[4]

3) S. Kitahara, *This Journal*, **30**, 109 (1960)
4) A. Olander and H. Liander, *Acta Chim. Scand.*, **4**, 1437 (1950)
5) W. T. Holser and G. C. Kennedy, *Am. J. Sci.*, **256**, 744 (1958)
6) C. S. Copeland, J. Silverman and S. W. Benson, *J. Chem. Phys.*, **21**, 12 (1953)

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Results and Considerations

The solubility in the three-phase field The results of the measurements are given in Table 3 and Fig. 1 together with the solubility in pure water. The solubility in aqueous sodium chloride solution agrees with the solubility in water until 240°C, and the former is higher than the latter above 280°C. The difference of the solubility between the two solvents increases with temperature. The effect of the concentration of sodium chloride on the solubility becomes greater with the concentration. The reproducible values are obtained in every measurement within the experimental error until 340°C, provided that the determinations are carried out under the

Table 3 Solubility of quartz in the three-phase field

Temp. °C	Press. atm	Time hr	Solubility weight %					Type of group
1% NaCl solution								
240	33	120	0.045		( ): Average value for			
280	63	96	0.057		the same group			
300	87	96	0.062					
320	113	48	0.065					
330	126	48	0.068	0.068	(0.068)			
340	145	24	0.077	0.081				
〃	〃	48	0.079		(0.079)			
350	164	24	0.075	0.072	(0.074)			
360	181	18	0.062	0.059	0.057	(0.059)		
370	203	18	0.053	0.056	(0.054)			lower
〃	〃	〃	0.093					higher
380	228	18	0.040	0.045	(0.043)			lower
〃	〃	〃	0.094					higher
3% NaCl solution								
240	332	120	0.042					
280	62	96	0.058					
300	84	96	0.066					
320	110	48	0.080	0.079	(0.079)			
340	140	24	0.085	0.082	0.079	(0.082)		
360	176	18	0.079	0.079	0.078	0.075	(0.078)	lower
〃	〃	〃	0.086					mediate
〃	〃	〃	0.102					higher
380	223	18	0.074	0.069	(0.072)			lower
〃	〃	〃	0.101	0.105	(0.103)			higher
400	276	18	0.061	0.058				
〃	〃	42	0.061		(0.060)			lower
〃	〃	18	0.099					
〃	〃	42	0.104		(0.102)			higher

(Table 3 *continued*)

Temp. °C	Press. atm	Time hr	Solubility weight %					Type of group
7% NaCl solution								
140	4	120	0		( ): Average value for			
160	6	120	0.008		the same group			
200	15	120	0.025					
240	32	120	0.044					
280	61	96	0.059					
300	80	96	0.066					
320	103	48	0.088	0.089	(0.089)			
340	133	24	0.096	0.098	0.101	(0.099)		
360	169	18	0.094	0.091	0.091	0.086	(0.091)	lower
〃	〃	〃	0.113	0.118	(0.116)			higher
380	214	18	0.084					lower
〃	〃	〃	0.101					mediate
〃	〃	〃	0.120	0.126	(0.123)			higher
400	271	18	0.096					lower
〃	〃	〃	0.109	0.103	(0.106)			mediate
〃	〃	〃	0.121	0.122	(0.122)			higher
420	310	18	0.122	0.126	0.120	0.123		higher

same conditions. However, at temperatures above 340°C the reproducible values are not always obtained in several determinations under the same conditions, namely the values are variable within a certain region. They are roughly classified into three groups, higher, lower and intermediate. The higher and lower values are shown as the solubility curves '*h*' and '*l*' respectively in Fig. 1, and as Table 3 shows, the tendency that the value belongs to either of these groups depends on the conditions of the measurements.

The reason why the solubility in aqueous sodium chloride solution is higher than in water will be due to the fact that the specific gravity of water in the liquid phase of sodium chloride solution is greater than that of pure water at the same temperature and sodium chloride affects on the equilibrium between silica and water. The former factor is expected from the fact that the solubility of quartz increases with the specific gravity of water at the same temperature as reported by G. C. Kennedy[7]. Although it is not determined what sort of equilibrium is reached for the solution of silica in water, C. S. Hitchen[8] has suggested that the equilibrium between molecular dispersion, collodial dispersion and a solid phase is reached. This can be represented by the following equation:

solid phase $\rightleftharpoons$ molecular dispersion $\rightleftharpoons$ colloidal dispersion.

Assuming that this equilibrium is attained in solution, when sodium chloride is added to this equilibrium system, the colloidal particles will be aggregated into larger particles, and the portion

7) G. C. Kennedy, *Econ. Geol.*, 45, 629 (1950)
8) C. S. Hitchen, *ibid.*, 40, 361 (1945)

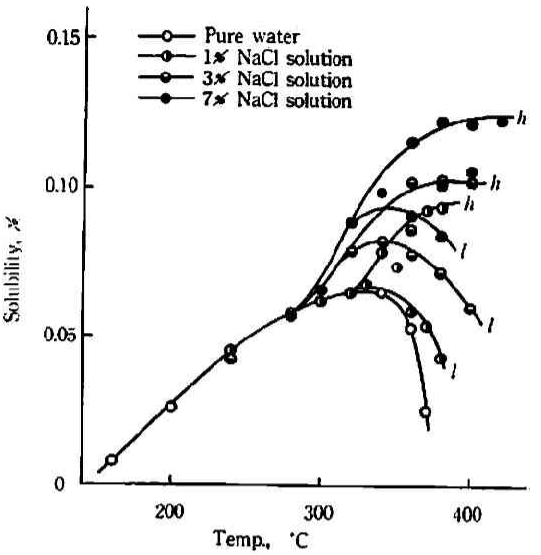

Fig. 1 Solubility curves in the three-phase field

of equilibrium under consideration will be shifted to the right, favoring the increase of colloidal dispersion. It seems that this causes the solution of quartz and consequently the solubility of quartz

Table 4 Solubility of quartz under the supercritical conditions

weight %

Pack. ratio ml/ml	Temp., °C / Conc., %	400	420	440	460	480	500
1/3	0	0.036	0.044	0.053	0.063	0.075	0.090
	1	0.046	0.056	0.068	0.085	0.105	0.125
	3		0.070	0.085	0.104	0.125	0.144
	7			0.120	0.140	0.164	0.187
1/2.4	0	0.052	0.063	0.075	0.092	0.111	0.130
	1	0.075	0.085	0.099	0.114	0.131	0.151
	3		0.094	0.111	0.130	0.150	0.173
	7			0.135	0.162	0.185	0.210
1/2	0	0.080	0.094	0.110	0.132	0.158	
	1	0.094	0.109	0.124	0.143	0.163	
	3		0.115	0.132	0.156	0.180	
	7			0.150	0.180	0.210	
1/1.8	0	0.103	0.120	0.140			
	1	0.113	0.128	0.145			
	3		0.134	0.153			
	7			0.163			
1/1.6	0	0.131	0.157				
	1	0.132	0.160				
	3		0.165				

in aqueous sodium chloride solution increases more than in water. For the explanation of the variation of the values of the measurements under the same conditions it is considered that something, for instance, impurity in the solution or some variation of mechanical conditions in the autoclave, causes the change of the phase equilibrium between silica and sodium chloride solution.

The solubility under the supercritical conditions The results of the measurements

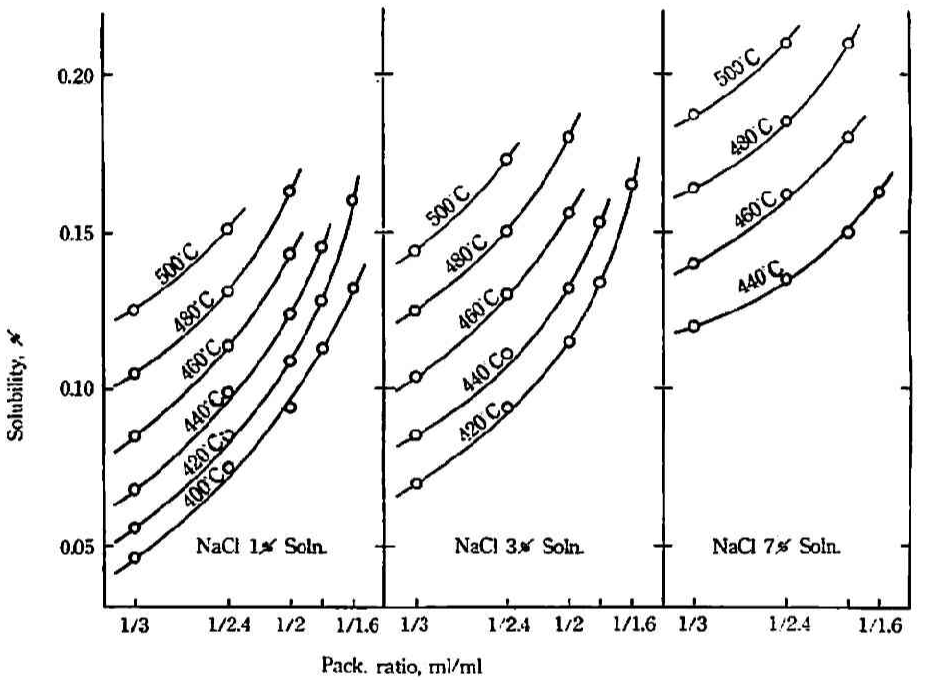

Fig. 2 Isothermal solubility curves under the supercritical conditions

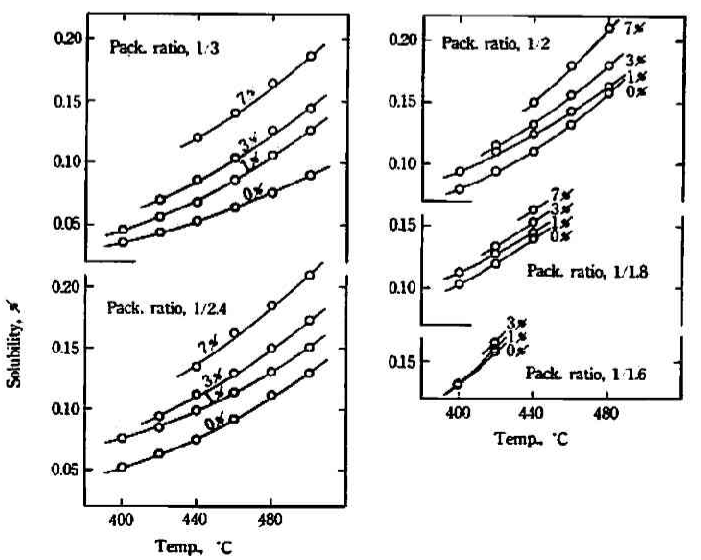

Fig. 3 Isovolumetric solubility curves under the supercritical conditions

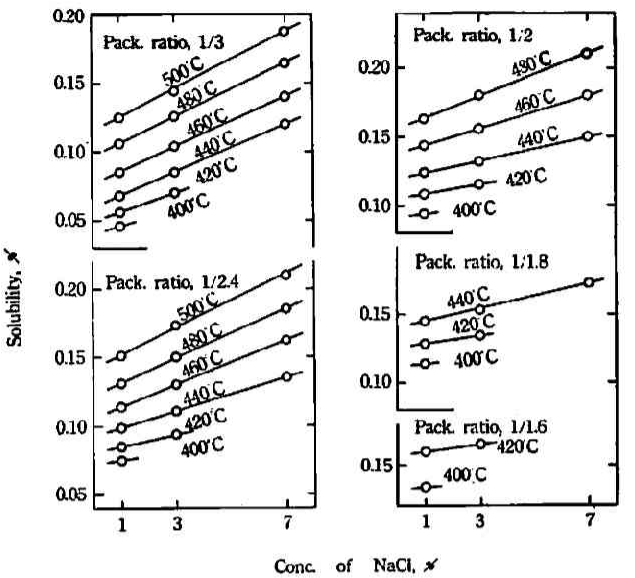

Fig. 4 Relations between solubility and concentration

are given in Table 4 together with the solubility in pure water. Figs. 2 and 3 show the isothermal solubility curves and the isovolumetric solubility curves respectively. The solubility under the supercritical conditions in sodium chloride solution as well as in the three-phase field is higher than in pure water. The solubility increases with increasing packing ratio of sodium chloride solution and with temperature. The effect of the concentration of sodium chloride on the solubility becomes greater with concentration, but smaller with increasing packing ratio, and negligibly small when packing ratio increases up to a certain value. Fig. 4 shows the solubility-concentration relations in each packing ratio. The relations at constant temperature are almost linear, and the gradient of the line becomes smaller with increasing packing ratio.

It is considered that sodium chloride affects the equilibrium of solubility of quartz in water, under supercritical conditions as well as in the three-phase field, but the mechanism of it can not be explained now.

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